LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

UCRL-JRNL-204519

Compressive and Tensile Stress in CdSe Semiconductor Quantum Dots

Robert W. Meulenberg, Travis Jennings, Geoffrey F. Strouse

Submitted to Physical Review B

June 7, 2004

Compressive and Tensile Stress in Colloidal CdSe Semiconductor Quantum Dots

Robert W. Meulenberg

Materials Science Division, Lawrence Livermore National Laboratory, Livermore CA 94550

Travis Jennings and Geoffrey F. Strouse

Department of Chemistry, Florida State University, Tallahassee, FL 32316

(Dated: May 18, 2004)

Abstract

Compressive and tensile stress in colloidal CdSe quantum dots (QDs) is examined using resonance Raman spectroscopy. We find that the dispersion of the longitudinal optical phonon mode with size does not follow theoretical calculations based on phonon confinement models. To account for these deviations, the presence of compressive or tensile stress in the QDs was proposed. We find that CdSe QDs prepared via a single source precursor (SSP) method exhibit compressive stress, while CdSe QDs prepared via high temperature lyothermal methods exhibit tensile stress. Evidence is provided that the SSP CdSe QDs stress is directly related to a surface effect.

PACS numbers: 63.22.+m

The role of surface reconstruction and its relationship to ligand passivation has been widely discussed as a critical factor in determining the optical properties of chemcially prepared semiconductor nanocrystals, or quantum dots (QDs).[1,2] The magnitude of surface reconstruction will depend on the surface energy of the QD, which is dictated by the size, shape, lattice ionicity, and surface passivation. Surface reconstruction at the inorganic/ organic interface can be envisioned as a surface pressure or tension term that can be measured by observation of the surface strain as a function of ligand passivant and QD size. Surface strain is readily probed by resonance Raman spectroscopy, providing a convenient method to analyze the size and ligand passivation dependent reconstruction of a QD.[3–5]

Semiconductor QDs are a class of solid-state materials whose physical properties are strongly dependent on the spatial dimensions of the particle.[6] For particle radii close to the Bohr exciton of the material, quantum confinement effects dominate the optical and electronic properties of these materials.[1] In addition to confinement effects, dimensional size effects can drastically alter the surface atom bonding[7] and passivant crystallinity[2] leading to surface reconstruction and lattice contraction, which can be related to the surface energy changing as a function of particle size.[8] What is not fully understood, however, is the change in the surface energy and lattice strain as the QD chemical synthesis is altered. An ideal experimental method to observe lattice strain is Raman spectroscopy.[9] For a dimensionally confined crystal, the competition between strain and confinement can have a drastic impact on the absolute energy of the optical phonons.[9] When the crystal experiences tensile stress or phonon confinement effects, the optical phonon energies shift to the red, while a crystal under compressive stress is expected to show a blue shift of the optical phonon. In this letter, shifts in the longitudinal optical (LO) phonon mode in CdSe QDs, measured by resonance Raman spectroscopy, is interpreted as arising from size dependent surface strain differences in ligand passivation in CdSe and CdSe/ZnS core-shell QDs. Interestingly, the strain, reported in terms of tensile and compressive stress, changes as a function of surface termination.

CdSe and CdSe/ZnS core-shell QDs were synthesized by known literature methods.[10,11] For the optical experiments, the samples were either pressed as a solid pellet, cast as a thin film, or dispersed in organic solvents.[12] The resonance Raman experimental set-up has been described elsewhere.[13] Laser powers of less than 60 mW were used to minimize sample degradation. Wavenumber calibration was obtained by using elemental sulfur and

argon lamps. A polarization descrambler was inserted prior to the entrance slit of the monochromater to avoid spectrometer polarization dependencies. The Raman spectra are not corrected for contributions from photoluminescence to minimize data distortion.

Figure 1 shows the size dependent resonance Raman spectra between 200-600 cm^{-1} of hexadecylamine (HDA) (Fig. 1a) and trioctylphosphine (TOPO) (Fig. 1b) coated CdSe QDs. The spectra consists of a strong mode centered at ~210 cm^{-1} arising from the LO phonon with a weaker mode arising from the second order LO (2LO) appearing at ~415 cm^{-1}.[14] The general trend of the data shows a softening of the LO phonon as particle size is decreased which can be attributed to phonon confinement (PC) effects and is consistent with previous Raman studies on CdSe QDs.[14–16] Intriguingly, a plot of the size dependent LO phonon peak for different samples produce a different magnitude of shift, suggesting a variance in the nature of the phonon confinement. As a result of PC, the phonon wave function becomes finite and therefore the $\mathbf{q} = 0$ is predicted to relax. This allows phonon modes from a wider range in the Brillouin zone to contribute to the Raman spectrum. The phonon wave function can be described as,

$$\Psi(q_o, r) = u(q_o, r)e^{iqr} \tag{1}$$

where $u(q_o, r)$ has the periodicity of the lattice. This allows PC effects on the phonon wavefunction to be expressed as,

$$\Psi(q_o, r) = W(r, L)\Psi(q_o, r) = \Psi'(q_o, r)u(q_o, r) \tag{2}$$

where $W(r, L)$ is a PC weighting function. If the perturbed wave function, Ψ', is expanded into a Fourier series, and if a Gaussian weighting function centered at q_o is considered, the Fourier coefficient becomes,

$$|C(0, \mathbf{q})|^2 \sim \exp(-L^2\mathbf{q}^2/\alpha^2) \tag{3}$$

where α is dependent on the crystal type. The one-phonon Raman spectra can then be calculated by,[17]

$$I(\omega, L) = \frac{L^3}{2\pi^{1/2}} \int_0^1 \frac{|C(0, \mathbf{q})|^2}{[\omega - \omega(\mathbf{q}]^2 + (\Gamma/2)^2} dq \tag{4}$$

where $\omega(\mathbf{q})$ is the bulk phonon dispersion relation and Γ is the natural linewidth. For CdSe, the bulk LO phonon dispersion relation is $\omega(\mathbf{q})$ = 213.1 (cm^{-1}) - 125.3$\mathbf{q}^2$ and Γ= 2 cm^{-1}.[18] This allows phonon confinement effects to be estimated quantitatively in terms

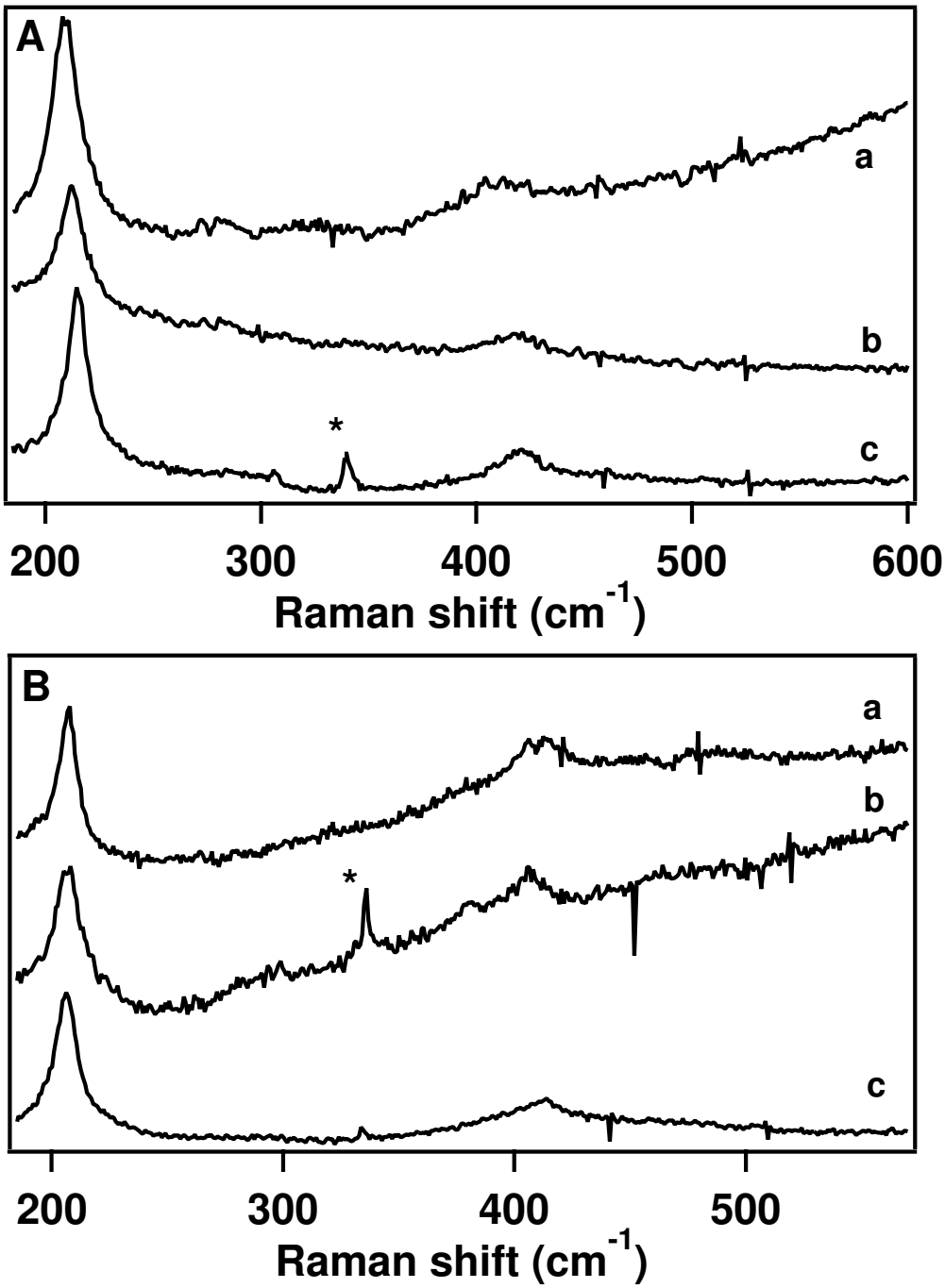

FIG. 1: Resonance Raman spectra (2.54 eV excitation) between 200-600 cm-1 of (A) HDA coated (a) 20, (b) 27.5, and (c) 30 Å and (B) TOPO coated (a) 35, (b) 25, and (c) 21.5 Å radius CdSe QDs. The asterisk (*) denotes laser plasma lines.

TABLE I: Theoretical and experimental LO phonon shifts from the bulk LO value. The CdSe radius in measured in Å, $\Delta\omega_{theory}$ is the difference between the calculated LO frequency based on the phonon confinement model and the bulk value in cm^{-1}, $\Delta\omega_{exp}$ is the difference between the experimental LO frequency and the bulk value in cm^{-1}, $\Delta\omega_{diff}$ is $\Delta\omega_{theory}$ - $\Delta\omega_{exp}$ in cm^{-1}, and P_{eff} is the effective pressure in GPa.

CdSe radius	$\Delta\omega_{theory}$	$\Delta\omega_{exp}$	$\Delta\omega_{diff}$	P_{eff}
30[a]	3.32	2.97	0.35	0.06
27.5[a]	4.02	3.81	0.21	0.03
20[a]	7.48	5.59	1.89	0.54
17[a]	10.36	7.70	2.66	0.76
35[b]	2.44	6.17	-3.73	-0.69
25[b]	4.42	7.00	-2.58	-0.42
24[b]	5.19	6.88	-1.69	-0.38
21.5[b]	6.78	8.97	-2.19	-0.62
25[c]	4.42	5.17	-0.75	-0.12
24[c]	5.19	5.06	-0.13	-0.03
21.5[c]	6.78	7.72	-0.34	-0.10

[a]HDA coated CdSe
[b]TOPO coated CdSe
[c]ZnS coated CdSe

of the phonon correlation length, L, which corresponds to the size of phonon confinement within the nanocrystal. The differences in the theoretical and experimental values are listed in Table I, where the theoretically predicted LO phonon shifts from the phonon confinement model are tabulated along with the observed experimental LO phonon shifts. The strain effects are reported as an effective compressive (positive) or tensile (negative) stress term. Although stress is a tensorial quantity,[19] the value for the stress listed in Table I represent spatially averaged stress due to the isotropic nature of the ordering of QDs in solution and films. The stress term can be related to size-dependent and ligand dependent reconstruction of the QD surface, and should also be dependent on particle sphericity as suggested by Baranov *et al.*[4]

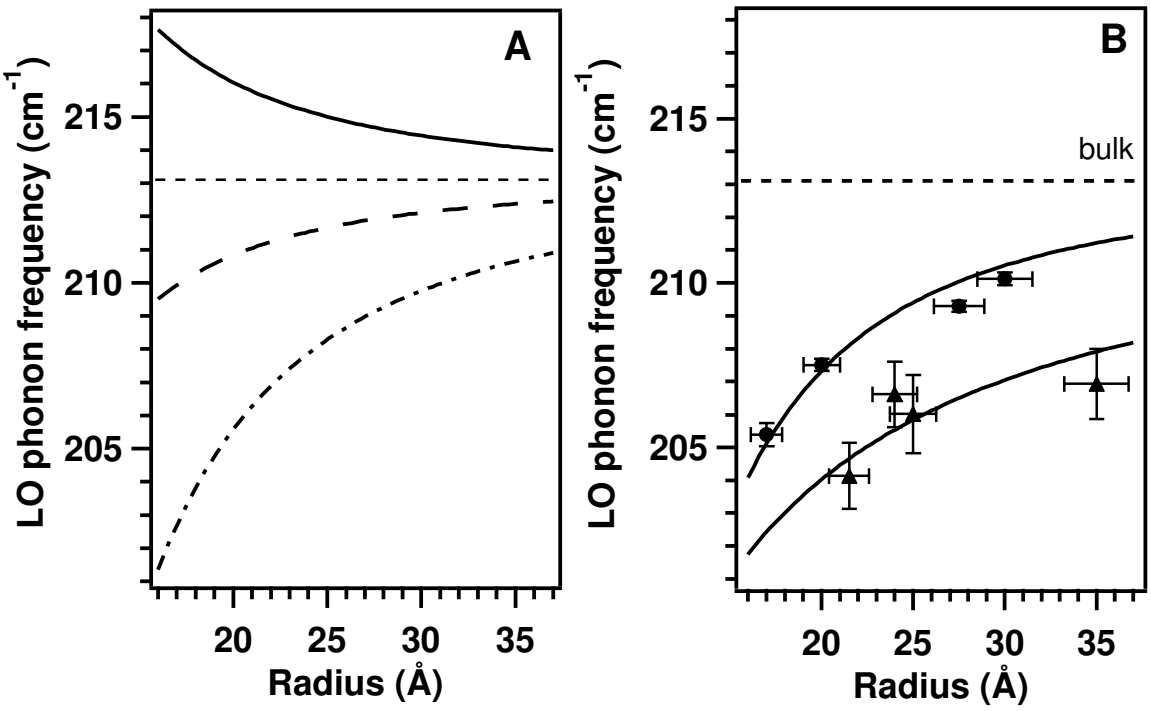

FIG. 2: (A) Calculation of the expected LO phonon dispersion. The various lines represent the theoretical LO dispersion based only on surface tension (solid), on phonon confinement (dashed-dot), on equal contribution from surface tension and phonon confinement (dotted). (B) Size dependent LO phonon for HDA (■) and TOPO (▲) coated CdSe QDs. The solid lines through the experimental points represent least squares fits of the points to a power law. The dotted line represents the bulk LO phonon frequency for CdSe.

Figure 2a plots the calculated LO phonon dispersion while Figure 2b plots the size dependent LO as a function of CdSe particle radius passivated with HDA and TOPO. As seen from the plot, the dispersion of the LO mode for the CdSe-HDA nearly tracks the calculated LO mode dispersion with a slight deviation at small particle sizes. The scaling law obtained from a power law fit of the data of the LO mode for the CdSe-HDA can be written as ω_{LO}=ω_o-2309*R^{-2} and is in agreement with the theoretical trend predicted for incorporation of a phonon confinement term (Figure 2) and is in agreement with the observed R^{-2} scaling law for CdSe QDs embedded in borosilicate glass.[16] The LO mode dispersion for the CdSe-TOPO follows a scaling law proportional to ω_{LO}=ω_o-181*R^{-1} and exhibits significant deviations from the theoretical values for the LO mode with phonon confinement taken into

account. Deviations between experimental and PC theoretical LO values may be explained by considering the effect of lattice strain which has been shown to impact the frequencies of the LO phonon modes. This interpretation has previously been used to describe the Raman spectra of CdSe QDs embedded in glass, as well as free standing CdSe QDs formed by high temperature pyrolysis of CdO.[3,16] To gain a more quantitative understanding on why the two passivants would exhibit such different physics, the effect of stress must be included in the analysis of the LO frequency data. The large deviation from PC theory may be an indication of glide plane or vacancy defects in the CdSe QDs grown in high temperature conditions, since it has been suggested that there exists stacking faults in the low-pressure phase of CdSe-TOPO QDs.[20] Possible reasons for this behavior are described below.

Figure 3 shows the compressive stress values obtained for the CdSe-HDA QDs as a function of particle radius. The dotted line in Fig. 3 represents the calculated surface stress obtained from,

$$P = \frac{2\gamma(R)}{R} \tag{5}$$

where $\gamma(R) = A + BR^{-2}$ and represents the size dependent surface tension[8] and R is the particle radius. The agreement between the theoretically derived surface stress term and the experimentally derived surface stress indicates that the compressive stress in the CdSe-HDA QDs is solely due to a surface effect and not from contributions arising form lattice disorder. The CdSe-TOPO samples on the other hand do not follow a smooth functional relationship implying that the size dependent tensile stress may not be related to a surface effect.

The difference between the passivants may provide insight into the experimental observation and a measure of the local molecular structure at the inorganic/organic interface. First, the CdSe-HDA samples show very little deviation from PC theory except for at small particle sizes indicating that these samples represent nearly defect free, strongly confined materials. This implies that the CdSe-HDA QDs behave similar to perfect spheres with very little influence from the HDA passivant layer. The HDA molecules may best be considered as a weakly physiorbed layer with possible π-donation to the inorganic surface. The CdSe-TOPO QDs, however, show a strong deviation from PC theory which may be best attributed to the strong π-backbonding interaction from the Cd d_π orbitals to the empty P p-orbitals inducing a surface reconstruction. This surface reconstruction is outward, owing to the tensile stress observed in the Raman experiments. It is expected that thiol passivated CdSe should show a LO phonon dispersion curve somewhere between the HDA and TOPO

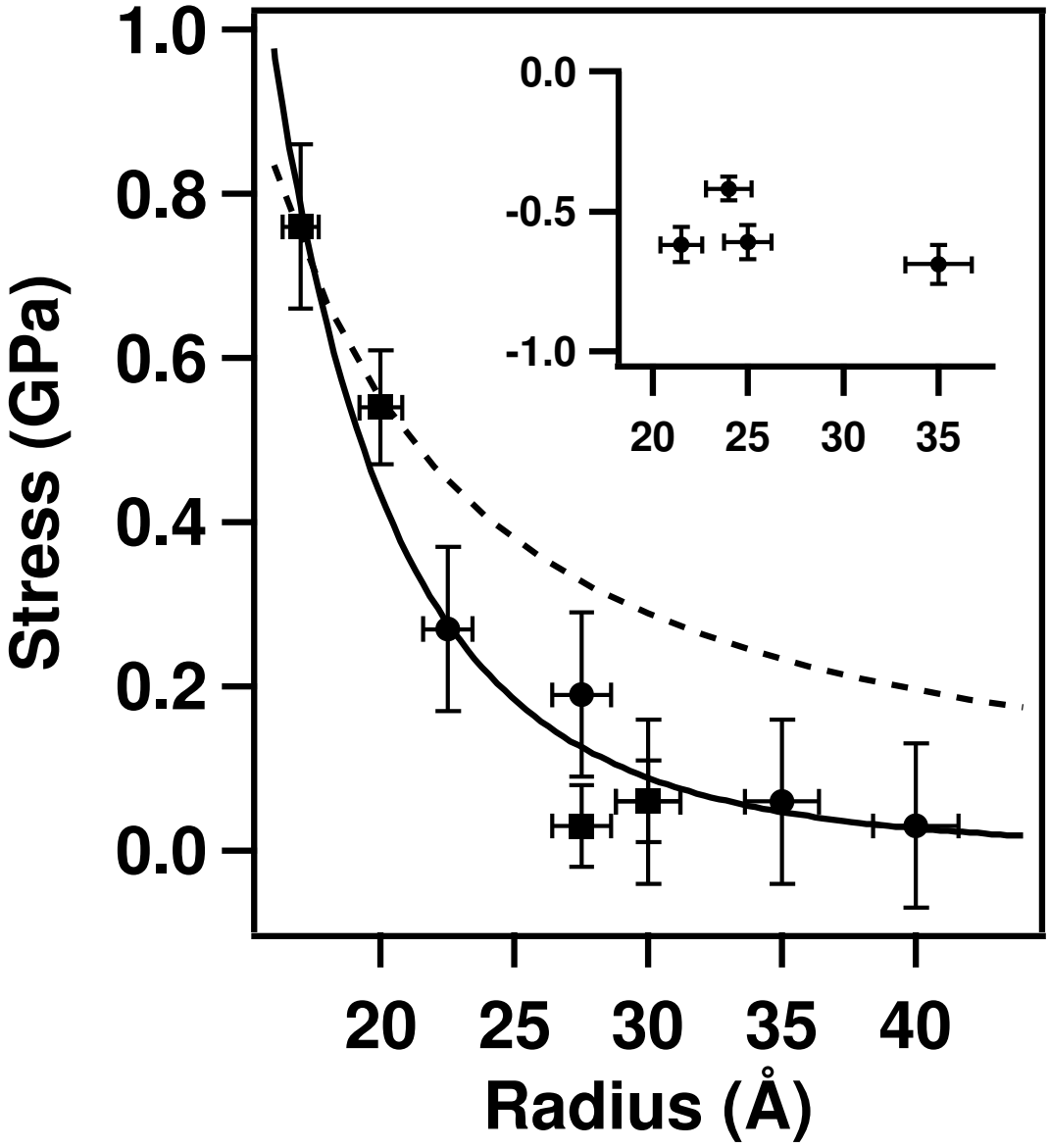

FIG. 3: Compressive stress as a function of particle size for CdSe-HDA QDs. The solid lines through the data points are a least squares fit of the data from this paper (•) and from Ref. 5 (■). The dotted line represents the calculated surface stress obtained from Eq. 5. The inset plots the size-dependent tensile stress for CdSe-TOPO QDs. Ordinate and abscissa are same in inset as in full spectra.

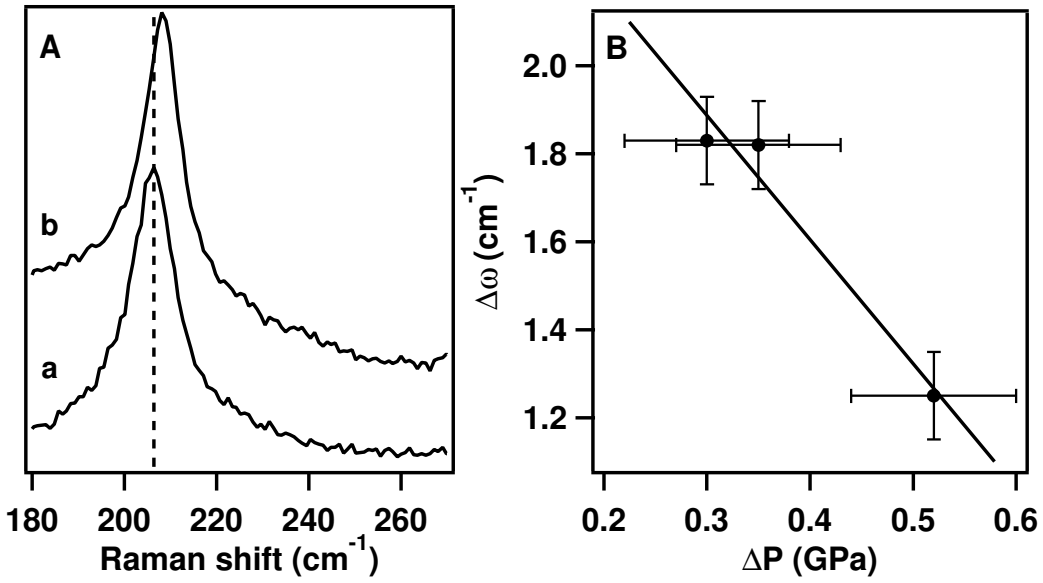

FIG. 4: (A) Comparison of 25 Å radius CdSe quantum dots passivated with (a) TOPO and (b) ZnS and (B) Change in LO phonon frequency versus change in pressure with addition of ZnS cap. Line is a guide for the eye.

coated QDs, as thiols are typically a weaker π-acceptor than phosphines.

To better understand the tensile stress in the CdSe-TOPO samples, the particles were passivated with an inorganic shell (ZnS) (Fig. 4). The lattice mismatch between CdSe and ZnS is $\sim$11 %, therefore we expect a large strain will occur at the interfacial region of the inorganic shell due to the lattice mismatch. Figure 4a shows the difference between $\sim$25 Å radius CdSe QDs passivated with TOPO and ZnS. Figure 4b plots the ZnS induced CdSe LO phonon shifts versus the change in effective pressure. The observed shift in the data in Fig. 4a is +2 cm-1. This corresponds to a compressive stress of 3.1 kbar (0.31 GPa). The observed compressive stress due to the ZnS shell for the 21.5 Å CdSe sample is 5.4 (0.54 GPa), which is significantly larger than the 25 Å QD. Initial Raman experiments on 18.5 Å CdSe/ZnS provide evidence that the ZnS induced compressive stress could reach nearly 1 GPa at small particle sizes. The larger values of compressive stress in the 18.5, 21.5, and 24 Å QDs indicate that the relative lattice mismatch between the core and shell is greater in the smaller QDs. This may be related to larger surface reconstruction on the smaller QDs from the strong phosphine-surface interaction. The larger values of compressive stress in

the smaller QDs indicates that the relative lattice mismatch between the core and shell is greater in the smaller QD. However, there exists more intriguing impact of the additional compressive stress term induced by the ZnS layer. From Table I, we see that the observed tensile stress for the TOPO and ZnS coated CdSe is very different, with a large range between CdSe-TOPO and CdSe-ZnS. It is therefore quite obvious from inspection of Table I that addition of the ZnS layer truly does energetically relax the surface of these nanoparticles. It should be noted, however, that the ability of the ZnS layer to sufficiently relax a QD surface will depend on the nature of the stress on the organically passivated particle.

In summary, compressive and tensile stress in CdSe QDs was studied by resonance Raman spectroscopy. The experiments prove that there exist distinct differences in the physics of QDs prepared by different chemical methods. These studies suggest that the differences in chemical preparation of QDs will greatly impact the future advance of device technology based on nanomaterials.

This work was supported by a NSF-CAREER Award (DMR-9875940) and a NSF Nanotechnology Grant (DMR-9871849) and performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

---

[1] A. P. Alivisatos, J. Phys. Chem. **100**, 13226 (1996).

[2] R. W. Meulenberg, S. Bryan, C. S. Yun, and G. F. Strouse, J. Phys. Chem. B **106**, 7774 (2002).

[3] J. Y. Zhang, X. Y. Wang, M. Xiao, L. Qu, and X. Peng, Appl. Phys. Lett. **81**, 2076 (2002).

[4] A. Baranov, Y. Rakovich, J. Donegan, T. Perova, R. Moore, D. Talapin, A. Rogach, Y. Masumotot, and I. Nabiev, Phys. Rev. B **68**, 165306 (2003).

[5] R. W. Meulenberg and G. F. Strouse, Phys. Rev. B **66**, 035317 (2002).

[6] N. F. Johnson, J. Phys.-Cond. Matt. **7**, 965 (1997).

[7] K. S. Hamad, R. Roth, J. Rockenberger, T. van Buuren, and A. P. Alivisatos, Phys. Rev. Lett. **83**, 3474 (1999).

[8] S. H. Tolbert and A. P. Alivisatos, Ann. Rev. Phys. Chem. **46**, 595 (1995).

[9] H. Rho, H. E. Jackson, S. Lee, M. Dobrowolska, and J. K. Furdyna, Phys. Rev. B **61**, 15641 (2000).

[10] S. L. Cumberland, K. M. Hanif, A. Javier, G. A. Khitrov, G. F. Strouse, S. M. Woessner, and C. S. Yun, Chem. Mater. **14**, 1576 (2002).

[11] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Amer. Chem. Soc. **115**, 8706 (1993).

[12] Crystallinity and size dispersity of the QDs are ∼5 % and are monitored by UV-Vis absorption, x-ray diffraction, and transmission electron microscopy analysis.

[13] R. W. Meulenberg and G. F. Strouse, Phys. Rev. B **66**, 035317 (2002).

[14] A. P. Alivisatos, T. D. Harris, L. E. Brus, and A. Jayaraman, J. Chem. Phys. **89**, 5979 (1988).

[15] A. P. Alivisatos, T. D. Harris, P. J. Carroll, M. L. Steigerwald, and L. E. Brus, J. Chem. Phys. **90**, 3463 (1989).

[16] Y. N. Hwang, S. H. Park, and D. Kim, Phys. Rev. B **59**, 7285 (1999).

[17] H. Kohno, T. Iwasaki, Y. Mita, and S. Takeda, J. Appl. Phys. **91**, 3232 (2002).

[18] C. Trallero-Giner, A. Debernardi, M. Cardona, E. Menendez-Proupin, and A. I. Ekimov, Phys. Rev. B **57**, 4664 (1998).

[19] F. Cerdeira, C. J. Buchenauer, F. H. Pollak, and M. Cardona, Phys. Rev. B **5**, 580 (1972).

[20] J. N. Wickham, A. B. Herhold, and A. P. Alivisatos, Phys. Rev. Lett. **84**, 923 (2000).